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POLYMER ELASTOMER MOLDED PRODUCT AND METHOD FOR USING IT  
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## Specification

### POLYMER ELASTOMER MOLDED PRODUCT AND METHOD FOR USING IT

#### Patent Claims

1. A method for using a polymer elastomer molded product wherein a deformation force is impressed on a polymer elastomer molded product at a temperature equal to or higher than its glass transition point and lower than its molding temperature, wherein the aforementioned deformation is fixed by cooling said polymer elastomer molded product at a temperature equal to or lower than its glass transition point, and wherein the original shape of said polymer elastomer molded product is restored at the time of its use by heating it at a temperature equal to or higher than its glass transition point and lower than its molding temperature.

2. A polymer elastomer molded product obtained by means of urethane elastomer synthesis from an isocyanate, a polyol, and a chain extending agent by designating the glass transition point in the vicinity of room temperature.

3. Detailed explanation of the invention

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<sup>1</sup> Numbers in the margin indicate pagination in the foreign text.

(Industrial application fields)

The present invention concerns a polymer elastomer molded product and a method for using it, and more specifically, it concerns a polymer elastomer the glass transition point of which has been designated in the vicinity of room temperature as well as a method for using a polymer elastomer molded product by taking advantage of the drastic changes of its physical properties beneath and above its glass transition point.

(Prior art)

It is known that polymer elastomers are each characterized by the existence of a glass transition point (hereafter abbreviated as "Tg") at which their physical properties (e.g., vertical elastic coefficient, etc.) come to vary by several to several hundred times, and as far as mechanisms used commonly for avoiding the variations of physical properties in the vicinity of the Tg within the operative temperature region are concerned, shoe bottoms, power transmission belts, tires, etc. which, in cases where their Tg values are designated by at extremely low temperatures of approximately -40 C, exhibit low-elasticity attributes even at low temperatures, which are characteristic of ordinary natural rubbers or synthetic rubbers, have been known as application products, and artificial wooden materials, eating utensils, etc. which, based on the designations of their Tg values at extremely high temperatures of approximately 10[0] ~ 110 C, exhibit

such attributes as high elasticity, abrasion, resistance, etc. even at high temperatures have also been known.

(Problems to be solved by the invention)

Incidentally, as far as the glass transition points and physical properties of polymer urethane elastomers are concerned, it is known that the corresponding parameters of urethane /2

elastomer can be freely designated by optimizing the types of constituent isocyanates, types of polyols, types of chain extending agents, their mixing ratios, presence or absence of annealing, etc. The present inventors then compiled research on the development of a utility method which, based on a mechanism which is unprecedented in the prior art, namely the designation of the T<sub>g</sub> of a polymer elastomer in the vicinity of a normal operative temperature, takes advantage of the variations of its physical properties underneath and above the aforementioned temperature, as a result of which the present invention has become completed.

(Mechanism for solving the problems)

The present invention concerns a utility method wherein a minor external deformation force is impressed on a polymer urethane elastomer at a temperature lower than its molding temperature and equal to or higher than its glass transition point by taking advantage of its peculiar physical property, namely low elasticity, and wherein the deformation of said polymer elastomer is then fixed by means of cooling at a

temperature lower than the glass transition point for enabling the use of its resultant physical property, namely high elasticity.

In other words, the present invention concerns a polymer elastomer molded product synthesized by the prepolymer method from an isocyanate, a polyol, and a chain extending agent by designating the glass transition point in the vicinity of room temperature as well as a method for using a polymer elastomer molded product wherein a deformation force is impressed at the aforementioned temperature equal to or higher than its glass transition point and lower than its molding temperature, wherein said deformation is fixed by means of cooling at a temperature lower than its glass transition point, and wherein the original shape of said polymer elastomer molded product is restored at the time of its use by heating it at a temperature equal to or higher than its glass transition point and lower than its molding temperature.

As far as the present invention is concerned, a polymer elastomer molded product is initially formed in a shape necessary for an actual use, and after it has subsequently been induced to deform at a temperature equal to or higher than the glass transition point of said polymer elastomer and lower than its molding temperature, its deformation is fixed by means of cooling at a temperature lower than the aforementioned glass transition point, as a result of which such attributes of the polymer elastomer as its high

elasticity, abrasion resistance, etc. become accessible within a temperature range lower than the glass transition point, whereas, in a case where it becomes heated once again at or above the glass transition point, its deformation automatically becomes cancelled, as a result of which the initial molded shape (or shape analogous to it) becomes restored, and furthermore, the low elasticity attribute of the elastomer becomes accessible within a temperature range higher than the glass transition point. Thus, various applications become conceivable within fields in which morphological variations are functionally required with regard to molded products which exhibit peculiarly different physical properties within its operative temperature region as well as methods for using them.

Any conceivable substances can be employed as the polymer elastomer that constitutes the molded product of the present invention so long as their  $T_g$  values coincide with the vicinity of the objective designation temperature, although elastomers which exhibit drastic elasticity variations beneath and above said  $T_g$  values are desirable, and as such, a polyurethane elastomer, styrene-butadiene elastomer, nitrile-butadiene elastomer, etc. are normally used.

Next, examples for manufacturing polyurethane elastomers endowed with various  $T_g$  values will be explained. There are no special restrictions on the isocyanate component to be used for manufacturing the polyurethane

elastomer so long as it is selected from among those which are used commonly for polyurethanes, and it may, for example, be instantiated by diphenylmethane diisocyanate, 2,4- or 2,6-toluylene diisocyanate, - or p-phenylene diisocyanate, isophorone diisocyanate, hexamethylene diisocyanate, their crude forms, and their mixtures.

Ones which possess at least two intramolecular hydroxyl groups, furthermore, are used as polyol components, and applicable ones may, for example, be instantiated by polyoxyalkylene polyols which are manufactured by adding alkylene oxides to initialization agents such as polyvalent alcohols (e.g., diols, triols, etc.), aliphatic amines, aromatic amines, etc.; polyester polyols which are manufactured by condensing acids and alcohols; polytetramethylene glycol; polybutadiene polyols; etc.

Chain extending agents or cross-linking agents are instantiated by glycols such as ethylene glycol, butane diol, diethylene glycol, etc., amines such as diethanolamine, triethanolamine, toluylenediamine, hexamethylenediamine, etc., polyisocyanates such as a TDI (toluylene diisocyanate) adduct of trimethylolpropane, triphenylmethane triisocyanate, etc./3

If necessary, furthermore, catalysts may also be used for the purpose of accelerating the reaction.

Such catalysts are instantiated by tertiary amines such as triethylamine, tetramethylpropylenediamine,



tetramethylhexamethylenediamine, toluylenediamine, etc. and metal catalysts which are represented by such tin-containing catalysts as stannous octoate, stannous oate, dibutyltin dilaurate, etc., and they may each be used alone or as mixtures.

A urethane elastomer is synthesized by using the aforementioned isocyanate, polyol, and chain extending agent as well as, if necessary, the catalyst(s) based on the prepolymer method.

Next, the method for synthesizing the urethane elastomer based on the prepolymer method will be explained.

First, the diisocyanate and polyol are mutually reacted at a specified mixing ratio ( $A = [\text{NCD}]/[\text{OH}]$  molar ratio), as a result of which a prepolymer becomes synthesized. After the reaction has become completed, the chain extending agent is added in such a way that a desired mixing ratio ( $B = [\text{chain extending agent}]/[\text{prepolymer}]$  molar ratio) will become achieved, and after the obtained mixture has subsequently been flowed into a defoaming mold, it is subjected to a cross-linking reaction for 1 or 2 days at a temperature of 60 C within a thermostat dryer, as a result of which a urethane elastomer becomes synthesized. The foregoing synthesizing operation may be carried out either in a solvent-containing system or solvent-free system.

The following are conceivable as factors which affect the  $T_g$  and other physical properties: 1): Types of isocyanates; 2): Types of polyols; 3): Types of chain

extending agents; 4): Mixing ratio A; 5): Mixing ratio B; 6): Annealing; etc. A urethane elastomer endowed with a desired Tg profile can be freely synthesized by manipulating these factors 1) through 6).

In the following, an actual embodiment in which the present inventors proceeded to prepare a urethane elastomer to be used in the present invention will be explained, although it goes without saying that it is not binding.

#### Embodiment

A prepolymer was synthesized by reacting 2,4-TDI (trademark: TDI 100, manufactured by Mitsubishi Kasei Corp.) as an isocyanate component together with a polyol (trademark: PP-10000, manufactured by Sanyo Kasei Co.) at a mixing ratio A (NCO/OH molar ratio) of 3.06 in a catalyst-free system. After the reaction had been completed, 1,4-butane diol was added as a chain extending agent in such a way that a mixing ratio B (OH/NCO (prepolymer) molar ratio) of 0.62 would be achieved, and the contents were agitated and reacted in a vacuum. After the obtained product had subsequently been flowed into a mold, it was cured at a temperature of [6]0 C over a 1-day period, as a result of which a molded product was obtained. The Tg value of said melting point was -5 ~ 0 C (Embodiment Nos. 2 ~ 4).

The respective Tg values of polyurethane elastomers synthesized by redesignating the compositions and mixing

ratios according to otherwise identical procedures are summarized in Tables I and II.

Table I

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Example No.	Prepolymer		A = [NCO] /[OH]	Chain extending agent	B = [Chain extending agent] /[pre- polymer]	Tg, C <sup>*6</sup>
	(A)	(B)				
1-1	(C)	BPX- S5 <sup>*1</sup>	0.6 2	(F)	6	51
1-2	(D)	(D)	0.6 2	(D)	18	10 7
1-3	(E)	P15- 20 <sup>*2</sup>	0.7 7	(D)	6	6
1-4	(D)	(D)	0.7 7	(D)	12	15
1-5	(F)	EPR- 100 <sup>*3</sup>	0.8 2	(D)	12	48
1-6	(C)	(D)	0.8 2	(D)	18	92
1-7	(E)	BPX- 38 <sup>*4</sup>	0.8 2	(D)	12	60
1-8	(D)	(D)	0.8 2	(D)	18	~ 122

[(A): Isocyanate; (B): Polyol; (C): Isophorone diisocyanate;  
 (D): Same as above; (E): Isophorone  
 diisocyanate/diphenylmethane diisocyanate = 1/1; (F): TDI  
 adduct of trimethylolpropane; (\*1): Polyol manufactured by  
 Asahi Denka Kogyo Co.; (\*2): Polyol manufactured by Asahi  
 Denka Kogyo Co.; (\*3): Polyol manufactured by Sanyo Kasei  
 Kogyo Co.; (\*4): Polyol manufactured by Asahi Denka Kogyo  
 Co.; (\*5): Reaction induced in a 50% solution of 4-methyl-2-  
 pentanone; (\*6): Measurement rendered by using a DSC  
 (differential scanning calorimeter) (average value)]

Table II

Example No.	Prepolymer		A = [NCO] /[OH]	Chain extending agent	B = [Chain extending agent] /[pre- polymer]	Tg, C <sup>*2</sup>
	(A)	(B)				
2-1	(C)	P = 1000 <sup>*1</sup>	3	(E)	0.6	-5
2-2	(D)	P = 1000	4	(D)	0.6	5
2-3	(D)	P = 1000	5.2	(D)	0.6	20
2-4	(D)	PP=1000 <sup>*3</sup>	3.0	(D)	0.62	-5 ~ 0
			6			

[(A): Isocyanate; (B): Polyol; (C): 2,4-toluylene diisocyanate; (D): Same as above; (E): 1,4-butane diol; (\*1): Polyol manufactured by Asahi Denka Kogyo Co.; (\*2): Measurement rendered by using a DSC (average value); (\*3): Polyol manufactured by Sanyo Kasei Kogyo Co.]

As Tables I and II clearly indicate, it becomes possible to

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select the Tg value freely based on the combination of the hard segment of the polyurethane elastomer (i.e., isocyanate and chain extending agent) and its soft segment (i.e., polyol). Likewise, the respective Tg values of the styrene-butadiene elastomer and nitrile-butadiene elastomer can also be selected freely by varying the ratios of their hard segments (i.e., styrene or nitrile) and soft segments (i.e., butadiene).

Next, methods for using the polymer elastomer obtained according to the aforementioned procedures will be concretely shown.

The temperature at which the polymer elastomer is induced to become deformed is equal to or higher than the glass transition point of said polymer elastomer and below its molding temperature. In a case where it is lower than the glass transition point, the deformation becomes instantaneously recovered [sic], whereas, in a case where it is equal to or higher than the molding temperature, a new shape becomes conferred on the molded product.

There are no special restrictions on methods for inducing the deformation, and the molded product may, for example, be induced to deform by using a proper tool or bare hands while it abides within an atmosphere the temperature of which is equal to or higher than the glass transition point (e.g., hot air, hot liquid, steam, etc.).

The resulting deformation can be fixed by means of cooling by simply lowering the temperature below the glass transition point immediately after the deformation, although it is also possible to induce a creep deformation at a temperature lower than the glass transition point.

It is possible to cancel the deformation of the molded product of the present invention and to induce specified variations of its morphological or physical properties by simply heating the molded product at a temperature lower than the molding temperature, as a result of which the deformation becomes automatically cancelled while the original shape is being restored, and physical properties peculiar to an elastomer become concomitantly exhibited.

The time required for the restoration of the original shape can, furthermore, be abbreviated by increasing the caloric capacity of heat per unit time or by simply elevating the temperature.

(Application examples)

#### Application Example 1

A method for using the molded product of the present invention will be explained with reference to Figure 1, which shows a plaster cast.

First, the molded product (1), which consisted of the polyurethane elastomer shown in the "1-5" row of Table I the  $T_g$  value of which was designated at 48 C (molding stage of (a) in Figure 1), was immersed in a 30 C warm water, and subsequently, it was induced to deform according to the illustration of (b) in Figure 1, as a result of which the state of (1') became achieved (thermal deformation and cooling fixation stages). An extremely minuscule impression force suffices for inducing the deformation, and therefore, a contiguous retention shape (arm portion (2) in the same figure) can be easily achieved. After the goal of contiguation has been achieved, the deformed shape is retained and left unattended at room temperature (35 C or lower), as a result of which the molded product (1') becomes cooled, and its contiguously formed shape becomes fixed. After this fixation stage, the vertical elastic coefficient of the obtained molded sheet at a temperature equal to or lower than the  $T_g$  is sufficiently higher than its vertical elastic coefficient above the  $T_g$ , due to which a high elasticity is achieved, and the corresponding portion remains securely fixed without being easily deformed.

In a case where a plaster cast formed by said molded sheet is released, furthermore, the plaster cast is heated with a hair dryer, etc., and upon the achievement of a

temperature equal to or higher than the  $T_g$ , the elasticity of the molded sheet becomes lowered while the molded shape (1) becomes concomitantly restored (heating and deformation cancellation stage (c) of Figure 1), as a result of which the molded sheet (1) can be easily released in a repeatedly re-usable state.

#### Application Example 2

The work fixation material (3) characterized by the structural manifestations shown in (a) ~ (c) of Figure 2 was prepared by using a molded product of the urethane elastomer shown in the "1-7" row of Table I the  $T_g$  value of which was designated at 68 C, which coincides with the vicinity of a normal operative temperature.

Figure 2 (a) shows the shape prevailing at the molding stage, where the molding shape coincides with an actual utility shape.

Next, it is heated at a temperature equal to or higher than the glass transition point, as a result of which the heated structure becomes induced to deform into the desired shape (3') convenient for its storage, transportation, etc., and it is then cooled and fixed [(b) in Figure 2]. It is heated once again at the time of its use, as a result of which the utility shape manifest at the molding becomes restored.

#### Application Example 3



The eating utensil (4) shown in Figures 3 (a) and (b) was prepared by using the urethane elastomer shown in the "1-6" column of Table I the T<sub>g</sub> value of which was designated at 92 C, which coincides with a normal operative temperature. Figure 3 (a) shows the molded and/or utility shape, whereas Figure 3 (b) shows the non-utility shape (4'), which has been obtained by thermally deforming and then cooling the former for fixing its deformed shape.

In a case where it is heated once again for canceling its /6 deformation, the shape of (4) shown in Figure 3 (a) becomes restored.

Such an eating utensil is advantageous in the sense that its storage space can be conserved during its non-use.

Incidentally, Figure 4 shows an example of the temperature (C)-vertical elastic coefficient (E) curve of the polymer elastomer of the present invention. It shows the relationships among the T<sub>g</sub>, desirable temperature range for inducing deformation, and the molding temperature T<sub>3</sub>.

(Effects of the invention)

As far as the polymer elastomer molded product of the present invention and its utility method are concerned, the T<sub>g</sub> value is designated in the vicinity of a normal operative temperature rather than at an extremely low or extremely high temperature, as in the prior art, based on which it becomes possible to take advantage of the drastic variations

of the physical properties of the polymer elastomer molded product underneath and above the Tg value, and accordingly, it can be used advantageously within fields which functionally require the variations of its physical properties within its operative temperature region.

#### 4. Brief explanation of the figures

Figures 1 (a) ~ (c), Figures 2 (a) ~ (c), and Figures 3 (a) and (b) are each diagrams provided for explaining application embodiments of the present invention.

Figures 1 (a) ~ (c) instantiates a plaster cast, where Figure 1 (a) shows the molding stage, whereas Figure 1 (b) shows the thermal deformation and cooling fixation stages, whereas Figure 1 (c) shows the thermal deformation cancellation stage.

Figures 2 (a) ~ (c) instantiates a work fixation material, where Figure 2 (a) shows the shape at the molding stage, whereas Figure 2 (b) shows the shape at the time of storage and transportation, whereas Figure 2 (c) shows the shape at the time of its use.

Figures 3 (a) and (b) instantiate an eating utensil, where Figure 3 (a) shows the molded and/or utility shape, whereas Figure 3 (b) shows its shape at the time of its non-use.

Figure 4 is a graph which shows the relationships among the temperature-vertical elastic coefficient (E) curve of

the polymer elastomer of the present invention, its glass transition point ( $T_g$ ), and its molding temperature ( $T_3$ ).

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[(1):  
Vertical  
elastic  
coefficient  
; (2):  
Temperature  
; (3):  
Temperature  
range over  
which the

deformation is fixed; (4): Temperature range over which the  
deformation is induced or temperature range over which the  
initial shape is restored; (5): Higher]

Procedural Amendment Report

/7  
December 26, Sho 60[1985]

Dear Judge Michiro Uga, Chief of the Patent Agency:

1. Display of the case

Patent Application No. Tokugan Sho 60[1985]-154598

2. Title of the invention

Polymer elastomer molded product and method for using  
it

3. Amending party

Relation to the case: Patent Applicant

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Name: (?179): Akira Uchida, patent attorney (and one other)

[Official seal, "Akira Uchida,  
Patent attorney"]

5. Date of amendment order: Spontaneous amendment

6. Number of inventions added as a result of the amendment:  
None

(60.12.2)

[Scratched stamp, "Patent Agency,  
60.8.26 ..."]

7. Objects of amendments

(1): "Detailed explanation of the invention" section of the specification

8. Contents of amendments

(1): "Stannous oate" in lines 7 ~ 8 of page 7 of the specification is amended as "stannous oleate."

(2): "PP-10000" in line 19 of page 8 of the same is amended as "PP-1000."

(3): "EPE-100" in the "polyol" row corresponding to Example No. 1-5 in Table I of page 10 of the same is amended as "BPE-100."

(4): "P = 1000" In the "polyol" rows corresponding to Example Nos. 2-1, 2-2, and 2-5 in Table II of page 11 of the same is amended as "P-1000."